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(54) A method for the manufacture of yellow azo-based pigments

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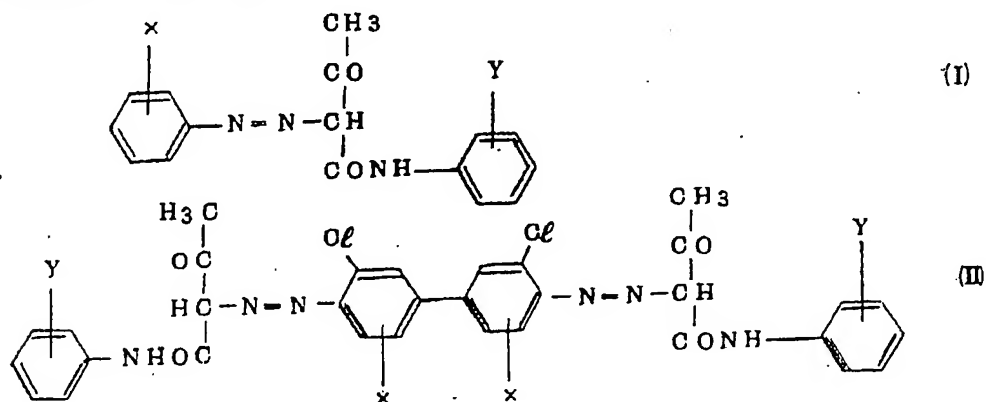
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Scope of the Patent Claim

A method for the manufacture of yellow azo-based pigments, characterized in that alkaline earth metal salts or organic amine salts of a sulphonic acid of pigment (I) or pigment (II), which can be represented by the general formulae indicated below, are mixed with pigment (I) or pigment (II) or a mixture of these pigments.



(X and Y in these formulae signify one or more substituent groups selected from among the group comprising H, CH₃, Cl, NO₂ and OCH₃.)

Detailed Description of the Invention

The invention concerns a method for the manufacture of yellow azo-based pigments which can be dispersed in a low viscosity non-aqueous vehicle and provide dispersions which have excellent fluidity.

Dispersions of the Fast Yellow-based pigments which can be represented by general formula (I) indicated below and the Benzidine Yellow-based pigments which can be represented by general formula (II) indicated below in a low-viscosity non-aqueous vehicle, such as paints and gravure inks and the like for example, sometimes exhibit a high viscosity, and there are cases where gelling occurs during prolonged storage and the materials become difficult to use.

(X and Y in these formulae signify one or more substituent groups selected from among the group comprising H, CH₃, Cl, NO₂ and OCH₃.)

The inventors have already recognized that the admixture of the sulphonic acid organic amine salts or sulphonic acid alkaline earth metal salts of the copper phthalocyanine-based pigments with copper

phthalocyanine-based pigments is very effective for preventing a rise in viscosity during storage of non-aqueous vehicle dispersions of copper phthalocyanine-based pigments (Japanese Examined Patent Publications S39-28884 and S40-4143). The present invention is an extension of this technology and provides a method for the manufacture of yellow azo-based pigments which have excellent fluidity as low viscosity non-aqueous vehicle dispersions of the abovementioned yellow azo-based pigments (I) and (II) with acetoacetoanilide as coupler, and with which there is virtually no rise in viscosity even on prolonged storage.

Thus, the present invention involves the admixture of a sulphonic acid alkaline earth metal salt or organic amine salt of a pigment which can be represented by general formula (I) or general formula (II), or a mixture of both (I) and (II). More precisely, it involves the admixture of a sulphonic acid alkaline earth metal salt or sulphonic acid amine salt of the azo-based pigment (I) or (II) with the pigments, or carrying out coupling by mixing a diazo component or coupler which has a sulpho group $-SO_3H$ as an intermediate of (I) or (II), which is to say in the diazo component or the coupler, and forming a lake of the dye with an alkaline earth metal salt or an organic amine.

If the amount of intermediate to which a sulpho group is bonded or pigment which has a sulphonic acid salt group which is admixed is too small then the effect of improving the fluidity of the dispersion is slight, and if the amount is too great then the alkali-resistance of the film which is produced is adversely affected, and so a suitable amount should be determined for each individual case, but in general the amount of pigment which has sulphonic acid salt groups is best selected within the range from 5 to 20 wt% with respect to the whole of the pigment. Furthermore, it is possible to control the hue, light resistance and solvent resistance of the target pigment by means of different combinations of the type of intermediate which has a sulpho group or pigment which has sulphonic acid salt group and different types of intermediate which do not have a sulpho group or pigment which does not have sulphonic acid salt groups. In this case as well the fluidity is improved in the same way, and illustrative examples are described below.

Example 1

3,3'-Dichlorobenzidine hydrochloric salt (58.7 g, 0.18 mol) was added to 200 cc of hot water and then 75 g (0.72 mol) of 35% hydrochloric acid were added and a solution was obtained, ice-water was added (liquid volume 2500 cc) and, while maintaining the liquid at a temperature of 0°C, 62 g of a 40% sodium nitrite aqueous solution (0.36 mol) were added and tetrazotization was achieved. Then 4 g of active carbon were added to decolorize the solution, the mixture was filtered, the excess nitrous acid was removed with sulphamic acid and tetrazotized solution (I) was obtained.

On the other hand, 2 g of sodium carbonate were dissolved in 200 cc of water at 50°C, 7.5 g (0.04 mol) of p-toluidine-m-sulphonic acid were added and dissolved and then 10.4 g (0.1 mol) of 35% hydrochloric acid were added and the p-toluidine-m-sulphonic acid was precipitated out. Ice-water was added to this (liquid volume 400 cc) and 6.9 g of 40% sodium nitrite aqueous solution (0.04 mol) was added while maintaining a liquid temperature of 5°C and diazotization was carried out, and the excess nitrous acid was removed with sulphamic acid and diazotized liquid (II) was obtained.

Separately, 48 g (1.2 mol) of caustic soda was dissolved in 2 l of water, 78 g (0.44 mol) of acetoacetoanilide were dissolved in the resulting solution, 80 g of 90% acetic acid were then added and ice-water was added to adjust the liquid temperature to 20°C and the liquid volume to 3 l, and a coupler solution was obtained. The abovementioned diazotized liquid (II) was added to this solution at from 5 to 10°C and coupling was carried out, and then the tetrazotized liquid (I) was added at from 0 to 5°C and coupling was carried out. After stirring the mixture for about 1 hour, the mixture was filtered and the precipitate was redispersed in 5 l of water, sodium carbonate was added and the pH was adjusted to from 8.0 to 8.5, and then 60 g of 10% barium chloride aqueous solution were added and, after heating to 80°C, the pigment was filtered off, washed with water and dried. Recovery 130 g.

Separately, for comparison, coupling was carried out in the conventional way with acetoacetoanilide and just the tetrazotized liquid (I) in the same way as described above, and a pigment with no sulphonic acid salt.

group was obtained.

The two pigments prepared in this way were each dispersed using a ball mill in a lime rosin-toluene based vehicle (solid fraction 55%) and the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 7%) with the pigment which contained the sulphonic acid salt groups was found to be considerably lower than that of the conventional product which did not contain sulphonic acid salt groups, as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

| | Pigment of the Invention | | Conventional Product | |
|------------------|--------------------------|----------------|----------------------|----------------|
| Rate of Rotation | When Prepared | After 3 Months | When Prepared | After 3 Months |
| 6 r.p.m. | 650 c.p.s. | 800 c.p.s. | 5240 c.p.s. | 6560 c.p.s |
| 12 | 387 | 550 | 2810 | 3820 |
| 30 | 225 | 320 | 1340 | 2650 |
| 60 | 158 | 250 | 722 | 2200 |

Example 2

A tetrazotized liquid (I) of 55.5 g (0.17 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt was prepared in the same way as in Example 1. On the other hand, a coupler solution was prepared in the same way as in Example 1 by adjusting an acetic acid solution of 65.5 g (0.37 mol) of acetoacetoanilide to a liquid temperature of 20°C and a liquid volume of 2 l. The tetrazotized liquid (I) was added to the coupler solution at from 0 to 5°C, coupling was carried out and a pigment slurry (II) was obtained. Separately, 3 g of sodium carbonate were dissolved in 300 cc of water at 60°C, 13.3 g (0.06 mol) of C-Acid (2-amino-4-methyl-5-chlorobenzenesulphonic acid) were dissolved in this solution and then 18.8 g (0.18 mol) of 35% hydrochloric acid were added and the C-Acid was precipitated out. Ice-water was added, the liquid temperature was set to 5°C and the liquid volume was set to 500 cc, 10.3 g (0.06 mol) of 40% sodium nitrite aqueous solution were added while maintaining the same temperature and diazotization was carried out, the excess nitrous acid was removed with sulphamic acid and diazotized liquid

(III) was obtained. Separately again, 6 g of caustic soda were dissolved in 300 cc of water, 12.6 g (0.066 mol) of acetoaceto-o-toluidide were dissolved in this solution, 10 g of 90% acetic acid were added and the toluidide was precipitated out, and the liquid temperature was adjusted to 25°C and the liquid volume was adjusted to 600 cc. The abovementioned diazotized liquid (III) was added to this liquid and, after coupling, the precipitate was filtered off and redispersed in 1.5 l of water and, after adjusting to pH from 8.0 to 8.5 with sodium carbonate, it was heated to 50°C, a solution obtained by dissolving 15 g of the acetic acid salt of palmitylamine in 100 cc of water was added and a lake was formed, and this was pigment lake (IV). This was added to the abovementioned pigment slurry (II), filtered off and dried. Recovery 132 g.

Separately, for comparison, coupling was carried out in the conventional way with acetoacetoanilide and just the tetrazotized liquid (I) in the same way as described above, and a pigment with no sulphonic acid salt groups was obtained.

These two pigments were each dispersed using a ball mill in a nitrocellulose-based vehicle (solid fraction 17%) and the viscosity (BM type rotation viscometer, 24°C) of the dispersion (pigment fraction 5.5%) which contained sulphonic acid salt groups was found to be considerably lower than that of the conventional product which did not contain sulphonic acid salt groups as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

| Rate of Rotation | Pigment of the Invention | | Conventional Product | |
|------------------|--------------------------|---------------------|----------------------|---------------------|
| | When Prepared | After 3 Months | When Prepared | After 3 Months |
| 6 r.p.m. 12 | 1580 c.p.s. 982 | 1780 c.p.s. 1130 | 4300 c.p.s. 2380 | 6200 c.p.s. 4300 |
| 30 r.p.m. 60 | 500 c.p.s. 338 | 620 c.p.s. 450 | 1160 c.p.s. 686 | 3200 c.p.s. 2560 |

Example 3

A tetrazotized liquid (I) was obtained in the same way as in Example 1

by tetrazotizing 65.2 g (0.2 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt and adjusting the liquid volume to 2.8 l and the liquid temperature to from 0 to 5°C. Separately, 40 g of caustic soda were dissolved in 2 l of water at 25 °C, 11.8 g (0.04 mol) of acetoacetosulphonic acid anilide potassium salt and 65.5 g (0.37 mol) of acetoacetoanilide were dissolved in this solution, 72 g of 90% acetic acid were added and the acetoacetoanilide was precipitated out, and the liquid volume was set to 2.8 l and the liquid temperature was set to 20 °C. The abovementioned tetrazotized liquid (I) was added to this and coupling was carried out and, after filtration, the precipitate was redispersed in 5 l of water, sodium carbonate was added to set the pH to from 8.0 to 8.5, and the dispersion was heated to 60°C and 40 g of a 10% calcium chloride aqueous solution were added to form a lake and, after stirring for 10 minutes, this was filtered off and dried. Recovery 128.5 g.

The pigment obtained in this way was dispersed with a ball mill in a lime rosin-toluene based vehicle (solid fraction 55%) in the same way as in Example 1 and the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 7%) was found to be considerably lower than that of the conventional product indicated in Example 1 as indicated below. Moreover, virtually no change in viscosity from the initial viscosity was seen when the pigment dispersion had been stored for 3 months.

| Rate of Rotation | When Prepared | After 3 Months |
|------------------|---------------|----------------|
| 6 r.p.m. | 430 c.p.s. | 490 c.p.s. |
| 12 | 400 | 450 |
| 30 | 370 | 410 |
| 60 | 350 | 390 |

Example 4

3,3'-dichlorobenzidine hydrochloric acid salt 9.8 g (0.03 mol) was tetrazotized in the same way as in Example 1 to prepare tetrazotized liquid (I). Separately, 19.5 g (0.066 mol) of acetoaceto-p-sulphonic acid anilide potassium salt was reprecipitated and a coupler liquid was obtained in the same way as in Example 3. Tetrazotized liquid (I) was added to this and coupling was carried out, the material was filtered off and washed with water

and then redispersed in 1.5 l of water, the pH was adjusted to from 8.0 to 8.5 with sodium carbonate and 60 g of 10% calcium chloride aqueous solution were added, while heating to 60°C, and a lake was formed, and this was taken as pigment slurry (II).

Separately, 3,3'-dichlorobenzidine was tetrazotized with sodium nitrite in the usual way and coupled with acetoaceto-o-toluidide in sodium acetate buffer solution to prepare pigment slurry (III). The abovementioned pigment slurry (II) (pigment content 34 g) was added to pigment slurry (III) (pigment content 300 g) and, after stirring, the pigment was filtered off and dried. Recovery 334 g.

When this pigment was dispersed in a lime rosin-toluene based vehicle (solid fraction 55%) in a ball mill, the viscosity of the dispersion (pigment fraction 7%) (BM type rotation viscometer, 25°C) was very low when compared with that of the conventional product indicated in Example 1; as indicated below. The viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

| Rate of Rotation | When Prepared | After 3 Months |
|------------------|---------------|----------------|
| 6 r.p.m. | 700 c.p.s. | 800 c.p.s. |
| 12 | 415 | 500 |
| 30 | 270 | 360 |
| 60 | 178 | 250 |

Example 5

35% hydrochloric acid 10.5 g (1.0 mol) was added to 58.7 g (0.34 mol) of 4-chloro-2-nitroaniline, ice-water was added and the liquid temperature was set to 0°C and the liquid volume was set to 2 l. A 40% sodium nitrite solution 58.6 g (0.34 mol) at the same temperature was added and diazotization was carried out, 7 g of active carbon were added and the mixture was decolorized and then filtered and the excess nitrous acid was removed with sulphamic acid and diazotized liquid (I) was obtained.

Separately, 65.5 g (0.37 mol) of acetoacetoanilide were added to 2 l of water at 25°C and dissolved, 61.2 g of 90% acetic acid were added and the material was reprecipitated, the liquid volume was adjusted to 2.5 l and the

liquid temperature was adjusted to 15°C and a coupler liquid was obtained.

The abovementioned diazotized liquid (I) was added to this coupler liquid and coupling was carried out, and pigment slurry (II) was obtained. Recovery 120 g. A slurry corresponding to 10 g of the pigment lake (IV) which was the palmitylamine salt of the coupling product of C-Acid and acetoaceto-o-toluidide indicated in Example 2 was added to the pigment slurry (II) obtained in this way and, after stirring, the pigment was filtered off and dried. Recovery 130 g.

Separately, for comparison, acetoacetoanilide was coupled with 4-chloro-2-nitroaniline in the usual way and a pigment which had no sulphonic acid salt groups was obtained.

When these two pigments were dispersed in a nitrocellulose-based vehicle based vehicle (solid fraction 17%) in a ball mill the viscosities (BM type rotation viscometer, 25°C) of the dispersions (pigment fractions 5.5%) were such that the viscosity of the pigment which contained sulphonic acid salt groups was very low when compared with that of the conventional product which did not have sulphonic acid salt groups, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

| | Pigment of the Invention | | Conventional Product | |
|------------------|--------------------------|----------------|----------------------|----------------|
| Rate of Rotation | When Prepared | After 3 Months | When Prepared | After 3 Months |
| 6 r.p.m. | 1220 c.p.s. | 1320 c.p.s. | 5560 c.p.s. | 7200 c.p.s. |
| 12 | 930 | 1030 | 3120 | 4600 |
| 30 | 475 | 560 | 1360 | 2850 |
| 60 | 325 | 405 | 870 | 2360 |

Example 6

4-Chloro-2-nitroaniline 69 g (0.4 mol) was diazotized in the same way as in Example 5 and diazotized liquid (I) was obtained.

On the other hand, 40 g of caustic soda was dissolved in 2 l of water at 25°C and then 11.8 g (0.04 mol) of the potassium salt of acetoaceto-p-sulphonic acid anilide and 65.5 g (0.37 mol) of acetoacetoanilide

were added and dissolved, and then 72 g of 90% acetic acid were added, the liquid volume was adjusted to 2.5 l, the liquid temperature was adjusted to 15°C and a coupler liquid was obtained. The abovementioned diazotized liquid (I) was added to this coupler liquid and coupled, and then the precipitate was filtered off and washed with water and then dispersed in 5 l of water, 40 g of 10% calcium chloride aqueous solution were added and a lake was formed, and the material was filtered off, washed with water and dried. Recovery 140 g.

When this pigment was dispersed in a nitrocellulose-based vehicle (solid fraction 17%) as shown in Example 5 in a ball mill the viscosity (BM type rotation viscometer, 25°C) of the dispersion (pigment fraction 5.5%) was very low when compared with that of the conventional product indicated in Example 5, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

| Rate of Rotation | When Prepared | After 3 Months |
|------------------|---------------|----------------|
| 6 r.p.m. | 1080 c.p.s. | 1180 c.p.s. |
| 12 | 970 | 1080 |
| 30 | 495 | 580 |
| 60 | 308 | 400 |

Example 7

4-Chloro-2-nitroaniline 62.1 g (0.36 mol) was diazotized in the same way as in Example 5, the liquid volume was adjusted to 2.5 l and the liquid temperature was adjusted from 0 to 5°C, and diazotized liquid (I) was obtained.

Separately, 6.9 g (0.04 mol) of sulphanilic acid were added to 200 cc of water, 2 g of sodium carbonate were added and the sulphanilic acid was dissolved at 50°C. 35% hydrochloric acid 12.5 g (0.12 mol) and ice-water were then added and the solution volume was adjusted to 300 cc and the liquid temperature was adjusted to 5°C and 7 g of a 40% sodium nitrite solution were added at the same temperature and diazotization was carried out and then the excess nitrous acid was removed with sulphamic acid. The

liquid volume was adjusted to 400 cc and the liquid temperature was adjusted to from 0 to 10°C and diazotized liquid (II) was obtained.

Caustic soda (40 g) was dissolved in 2 l of water and then 76 g (0.43 mol) of acetoacetoanilide were added and dissolved, 72 g of 90% acetic acid were added and the anilide was precipitated and then the liquid volume was adjusted to 2.5 l and the liquid temperature was adjusted to 15°C. The abovementioned diazotized liquid (II) was added to this liquid and coupling was carried out, and then the abovementioned diazotized liquid (I) was added and coupling was carried out. The precipitate was filtered off and washed with water and then redispersed in 5 l of water, sodium carbonate was added and the pH was adjusted to from 8.0 to 8.5 and then the dispersion was heated to 85°C, 60 g of 10% calcium chloride aqueous solution were added and a lake was formed, and the material was filtered off, washed with water and dried. Recovery 137 g.

Separately, for comparison, just acetoacetoanilide was coupled with 4-chloro-2-nitroaniline in the usual way and a pigment was obtained.

When these two pigments were dispersed in a lime rosin-toluene based vehicle based vehicle (solid fraction 17%) in a ball mill the viscosities (BM type rotation viscometer, 25°C) of the dispersions (pigment fractions 7%) were such that the viscosity of the pigment which contained sulphonic acid salt groups was very low when compared with that of the conventional product which did not have sulphonic acid salt groups, as indicated below. Moreover, the viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

| Rate of Rotation | Pigment of the Invention | | Conventional Product | |
|------------------|--------------------------|----------------|----------------------|----------------|
| | When Prepared | After 3 Months | When Prepared | After 3 Months |
| 6 r.p.m. | 1700 c.p.s. | 1810 c.p.s. | 3760 c.p.s. | 5770 c.p.s |
| 12 | 10800 | 1180 | 3010 | 5020 |
| 30 | 476 | 570 | 1030 | 3040 |
| 60 | 320 | 400 | 576 | 2180 |

Example 8

A tetrazotized liquid (I) of 55.5 g (0.17 mol) of 3,3'-dichlorobenzidine hydrochloric acid salt was obtained in the same way as in Example 1. Furthermore, an acetic acid solution of 65.5 g (0.37 mol) of acetoacetoanilide was adjusted to a liquid temperature of 20°C and a liquid volume of 2 l and a coupler liquid was obtained in the same way as in Example 1. The tetrazotized liquid (I) was added to this at from 0 to 5°C and coupling was carried out, and pigment slurry (I) was obtained.

Separately, 3 g of sodium carbonate were dissolved in 300 cc of water and dissolved at 60°C, 12 g (0.06 mol) of 3-amino-4-methoxybenzenesulphonic acid were dissolved in the solution and then 18.8 g (0.18 mol) of 35% hydrochloric acid were added and the abovementioned sulphonic acid was precipitated out. Ice-water was added and the liquid temperature was set to 5°C and the liquid volume was set to 50 cc and 10.3 g (0.06 mol) of 40% sodium nitrite aqueous solution were added while maintaining the same temperature and diazotization was carried out, the excess nitrous acid was removed with sulphamic acid and diazotized liquid (III) was obtained. Furthermore, separately, 6 g of caustic soda were added to 300 cc of water and dissolved, 12.6 g (0.066 mol) of acetoaceto-o-toluidide were dissolved in the solution, 10 g of 90% acetic acid were added and the toluidide was precipitated out, and the liquid volume was adjusted to 600 cc and the liquid temperature was adjusted to 25°C. The abovementioned diazotized liquid (III) was then added to this liquid, and then the precipitate was filtered off and redispersed in 1.5 l of water and, after adjusting the pH to from 8.0 to 8.5 with sodium carbonate, the mixture was heated to 50°C and a solution obtained by dissolving 9.2 g of aniline sulphuric acid salt in 100 cc of water was added and a lake was formed, and pigment lake (IV) was obtained. This was added to the abovementioned pigment slurry (II), filtered and dried. Recovery 125 g.

When this pigment was dispersed in a nitrocellulose-based vehicle (solid fraction 17%) in a ball mill the viscosity (BM type rotation viscometer, 25 °C) of the dispersion (pigment fraction 5.5%) was very low when compared with that of the conventional product indicated in Example 2, as indicated

below. The viscosity on storing this pigment dispersion for 3 months showed virtually no change from the initial viscosity.

| Rate of Rotation | When Prepared | After 3 Months |
|------------------|---------------|----------------|
| 6 r.p.m. | 1600 c.p.s. | 1900 c.p.s. |
| 12 | 1010 | 1120 |
| 30 | 600 | 700 |
| 60 | 420 | 460 |

⑤日本分類

23 D 1

24 A 5

23 D 3

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(全6頁)

1

2

④黄色アゾ系顔料の製造法

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②特願 昭40-35740

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5 東京都中央区京橋2の6の6の6

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同 柏岡暁

発明の詳細な説明

同所

本発明は低粘度非水性ビヒクルに分散させ、流

同 玉井厚

10 動性の優れた分散体を与える黄色アゾ系顔料の製造法に関する。

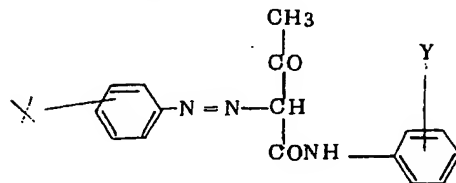
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同 山口健

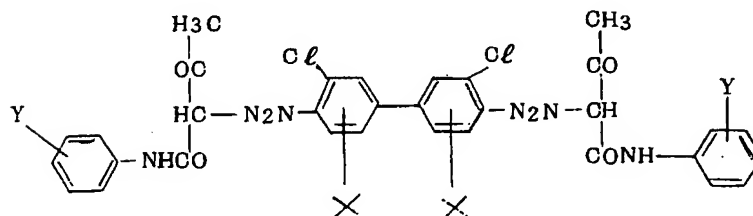
同所

一般式Iで表わされるファストエロー系顔料お

※ よびIIIで表わされるベンジジンエロー系顔料の低



(I)



(III)

(但し、式中XおよびYはH、CH₃、Cl、NO₂およびOCH₃の群から選ばれた1個以上の置換基を意味する)

の低粘度非水性ビヒクル中での分散体、たとえば塗料およびグラビアインキなどは往々高粘度を示し、長期間の貯蔵中ゲル化を生じ、使用困難となる場合がある。

本発明者らは、さきに銅フタロシアニン系顔料の非水性ビヒクル分散体の貯蔵中の粘度上昇を防止するため、銅フタロシアニン系顔料にそれらの

スルホン酸アルカリ土金属塩またはスルホン酸有機アミン塩を混合するのが極めて有効であることを認めた(特公昭39-28884および昭40-4143)。本発明はこの技術をさらに拡張したもので、アセトアセトアリドをカップラーとする上記黄色アゾ系顔料(I)および(III)を低粘度非水性ビヒクル分散体として、優れた流動性を有し、

長期間貯蔵してもほとんど粘度上昇することのない黄色アゾ系顔料の製造法を提供するものである。

すなわち本発明は一般式(I)もしくは(II)で表わされる顔料またはそれらの混合物に(I)または(II)のスルホン酸のアルカリ土金属塩または有機アミン塩を混有せしめることである。さらに詳言すれば、アゾ系顔料(I)または(II)にそれらのスルホン酸アルカリ土金属塩またはスルホン酸有機アミン塩を混合するか、あるいは(I)または(II)の中間体すなわちジアゾ成分またはカップラーにスルホン基-SO₃Hを有するジアゾ成分またはカップラーを混合してカップリングを行い、得られた染料をアルカリ土金属塩または有機アミンでレーキ化することである。

スルホン基を結合する中間体またはスルホン酸塩基を有する顔料の混合量は、過少ならば分散体の流動性向上に効果少く、過大ならば生成被膜の耐アルカリ性を阻害するので、その適量は個々の場合について決定すべきであるが、一般に完全全顔料に対しスルホン酸塩基を有する顔料が5～20重量%となるように選定するのがよい。また、スルホン基を有する中間体またはスルホン酸塩基を有する顔料の種類とスルホン基を有しない中間体またはスルホン酸塩基を有しない顔料と異種に組合せることにより、目的とする顔料の色相、耐光性および耐溶剤性を調整することができる。この場合も同様に流動性を向上する、つぎに実施例を示す。

実施例 1

熱湯200 cc に3,3'-ジクロロベンジジン塩基5.87 g (0.18モル)を加え、つぎに35%塩酸7.5 g (0.72モル)を加えてこれを溶解し、氷水を加えて(液量2500 cc)液温を0℃に保ちつつ40%亜硝酸ナトリウム水溶液6.2 g (0.36モル)を一度に加えてテトラゾ化する。これに活性炭4 gを加えて脱色、濾過し過剰の亜硝酸をスルファミン酸で消去しこれをテトラゾ化液(I)とする。

一方炭酸ナトリウム2 gを水200 cc 中に50℃で溶解し、これにP-トリイジン-m-スルホン酸7.5 g (0.04モル)を加えて溶解し、つぎに35%塩酸1.04 g (0.1モル)を加えてP-トリイジン-m-スルホン酸を析出せしめる。これに氷水を加えて(液量400 cc)液温5℃に保ちつつ、40%亜硝酸ナトリウム水溶液6.9 g 45

(0.04モル)を加えてジアゾ化し過剰の亜硝酸をスルファミン酸で消去しこれをジアゾ化液(II)とする。

別に水2ℓにカ性ソーダ48 g (1.2モル)を溶解し、これにアセトアセトアニリド78 g (0.44モル)を溶解し、90%酢酸80 gを加え、氷水を加えて液温20℃、液量3ℓに調整し、カップラー液とする。この液に上記ジアゾ化液(II)を5～10℃で加え、カップリングを行い、ついでテトラゾ化液(I)を0～5℃で加えてワップリングを行う。約1時間かきまぜた後濾過し、沈殿を5ℓの水に再分散し、炭酸ナトリウムを加えてPH 8.0～8.5に調整し、ついで10%塩化バリウム水溶液60 gを加え、80℃に加熱後、濾過水洗、乾燥する。収量130 g。

別に比較のため従来法に従い、上記と同一要領でアセトアセトアニリドとテトラゾ化液(I)のみをカップリングさせ、スルホン酸塩基を含有しない顔料を作る。

このようにして作製した両顔料をそれぞれライムロジントルエン系ビヒクル(固形分55%)にボールミルで分散させたときの分散体(顔料分7%)の粘度(BM型回転粘度計、25℃)はつぎのようにスルホン酸塩基を含有する顔料はスルホン酸塩基を含有しない従来品に比べ、著しく低粘度である。なお本顔料分散体を3カ月間貯蔵したときの粘度は初期粘度とほとんど変化は認められない。

| 回転数 | 本 顔 料 | | 従 来 品 | |
|----------|------------|------------|-------------|-------------|
| | 調製時 | 3 カ月後 | 調製時 | 3 カ月後 |
| 6 r.p.m. | 650 c.p.s. | 800 c.p.s. | 5240 c.p.s. | 6560 c.p.s. |
| 12 | 387 | 550 | 2810 | 3820 |
| 30 | 225 | 320 | 1340 | 2650 |
| 60 | 158 | 250 | 722 | 2200 |

実施例 2

例1と同じ要領で3.3'-ジクロルベンジジン塩酸塩55.5g(0.17モル)のテトラゾ化液(I)をつくる。一方例1と同じ要領でアセトアセトアニライド65.5g(0.37モル)の酢酸溶液を液温20℃、液量2ℓに調整しカッブラー液とする。これにテトラゾ化液(I)を0〜5℃で加えてカッブリングを行い、顔料スラリー(II)を得る。別に水300ccに炭酸ナトリウム3gを60℃で溶解し、これにC-酸(2-アミノ-4-メチル-5-クロルベンゼンスルホン酸)13.3g(0.06モル)を溶解し、ついで35%塩酸18.8g(0.18モル)を加えてC-酸を析出させる。水を加えて液温5℃、液量500ccとし、同温度に保ちながら40%亜硝酸ナトリウム水溶液10.3g(0.06モル)を加えてジアゾ化し、過剰の亜硝酸をスルファミン酸で消去し、ジアゾ化液(III)とする。また別に水300ccにカ性ソーダ6gを加えて溶解し、これにアセトアセト-オ-トルイダイド12.6g(0.066モル)を溶解し90%酢酸10gを加えてトルイダイドを析出さ

☆せ、液温25℃、液量600ccに調整する。この液に上記ジアゾ化液(III)を加えてカッブリング後、濾過し、沈殿を1.5ℓの水に再分散し、炭酸ナトリウムでPH8.0〜8.5に調整後50℃に加熱し、パルミチルアミンの酢酸塩15gを水100ccに溶解した液を加えてレーキ化し、顔料レーキ(IV)とする。これを上記顔料スラリー(II)に加え、濾過、乾燥する。収量132g。

別に比較のため常法に従い上記と同一要領でアセトアセトアニライドとテトラゾ化液(I)のみをカッブリングさせ、スルホン酸塩基を有しない顔料を作る。

これら両顔料をニトロセルロース系ビヒクル(固形分17%)にボールミルで分散させたときの分散体(顔料分5.5%)の粘度(BM型回転粘度計、24℃)は、つぎのように、スルホン酸塩基を含有する顔料は、スルホン酸塩基を含有しない従来品に比べ、著しく低粘度である。なお本顔料分散体を3カ月間貯蔵したときの粘度は初期粘度とほとんど変化は認められない。

| 回転数 | 本 顔 料 | | 従 来 品 | |
|----------|-------------|-------------|-------------|-------------|
| | 調製時 | 3 カ月後 | 調製時 | 3 カ月後 |
| 6 r.p.m | 1580 c.p.s. | 1780 c.p.s. | 4300 c.p.s. | 6200 c.p.s. |
| 12 | 982 | 1130 | 2380 | 4300 |
| 30 r.p.m | 500 c.p.s. | 620 c.p.s. | 1160 c.p.s. | 3200 c.p.s. |
| 60 | 338 | 450 | 686 | 2560 |

実施例 3

例1と同じ要領で3.3'-ジクロルベンジジン塩酸塩65.2g(0.2モル)をテトラゾ化し、液量2.8ℓ、液温0〜5℃に調整しテトラゾ化液(I)とする。別に水2ℓに25℃でカ性ソーダ40gを溶解し、これにアセトアセト-p-スルホン酸アニライドカリウム塩11.8g(0.04モル)およびアセトアセトアニライド65.5g(0.37モル)を溶解し、90%酢酸72gを加えてアセト

アセトアニライドを析出せしめ液量2.8ℓ、液温20℃とする。これに上記テトラゾ化液(I)を加えてカッブリングを行い、濾過後沈殿を5ℓの水中に再分散し、炭酸ナトリウムを加えてPH8.0〜8.5とし60℃に加熱し、10%塩化カルシウム水溶液40gを加えてレーキ化し10分かきまぜたのち、濾過、乾燥する。収量128.5g。

このようにして得られた顔料を例1と同じようにライムロジントルエン系ビヒクル(固形分55

(%)にボールミルで分散(顔料分7%)させたときの分散体の粘度(BM型回転粘度計、25℃)は、つぎのように例1に示した従来品と比べて著しく低く、また構造粘性をほとんど示さずニュートン流動に近い流動性を示している。また本顔料分散体を3カ月間貯蔵したときの粘度は、初期粘度とほとんど変化は認められない。

| 回転数 | 調製時 | 3カ月後 |
|----------|------------|------------|
| 6 r.p.m. | 430 c.p.s. | 490 c.p.s. |
| 12 | 400 | 450 |
| 30 | 370 | 410 |
| 60 | 350 | 390 |

実施例 4

例1と同じ要領で3,3'-ジクロロベンジジン塩酸塩9.8g(0.03モル)をテトラゾ化し、これをテトラゾ化液(I)とする。別に例3と同じ要領で、アセトアセト-p-スルホン酸アニライドカリウム塩19.5g(0.066モル)を再沈殿させてカップラー液をつくる。これにテトラゾ化液(I)を加えてカップリングを行い、濾過、水洗後、水1.5ℓ中に再分散し、炭酸ナトリウムでpH 8.0~8.5に調整し、60℃に加熱しながら10%塩化カルシウム水溶液60gを加えてレーキ化し顔料スラリー(II)とする。

別に3,3'-ジクロロベンジジンを常法のごとく亜硝酸ソーダでテトラゾ化しこれを酢酸ソーダの緩衝溶液中でアセトアセト-o-トルイダイドとカップリングを行い、顔料スラリー(III)をつくる。顔料スラリー(III)(顔料分300g)に上記顔料スラリー(II)(顔料分34g)を加え、かき混ぜた後濾過して乾燥する。収量334g。

本顔料をライムロジントルエン系ビヒクル(固形分55%)にボールミルで分散(顔料分7%)させたときの分散体の粘度(BM型回転粘度計、25℃)は、つぎのように例1に示した従来品と比べて著しく低粘度である。また本顔料の分散体を3カ月間貯蔵したときの粘度は、初期粘度とほとんど変化は認められない。

| 回転数 | 調製時 | 3カ月後 |
|----------|------------|------------|
| 6 r.p.m. | 700 c.p.s. | 800 c.p.s. |
| 12 | 415 | 500 |
| 30 | 270 | 360 |
| 60 | 178 | 250 |

実施例 5

4-クロロ-2-ニトロアニリン58.7g(0.34モル)に35%塩酸10.5g(1.0モル)を加え、氷水を加えて液温0℃、液量2ℓとする。これに同温度で40%亜硝酸ナトリウム水溶液58.6g(0.34モル)を加えてジアゾ化し、活性炭7gを加えて脱色後濾過し、過剰の亜硝酸をスルファミン酸で消去しジアゾ化液(I)とする。

別に水2ℓに25℃でアセトアセトアニライド65.5g(0.37モル)を加えて溶解し、90%酢酸61.2gを加えて再析出させ、液量2.5ℓ、液温15℃に調整してカップラー液とする。

このカップラー液に上記ジアゾ化液(I)を加えてカップリングを行い、顔料スラリー(II)をつくる。

収量120g。このようにして得られた顔料スラリー(II)に、例2に示したc酸とアセトアセト-o-トルイダイドのカップリング生成物のパルミチルアミン塩である顔料レーキ(IV)10gに相当するスラリーを加え、かき混ぜたのち、濾過、乾燥する。収量130g。

別に比較のため、常法に従い、4-クロロ-2-ニトロアニリンとアセトアセトアニライドをカップリングさせ、スルホン酸塩基を有しない顔料をつくる。

これら両顔料をニトロセルロース系ビヒクル(固形分17%)にボールミルで分散させたときの分散体(顔料分5.5%)の粘度(BM型回転粘度計、25℃)は、つぎのように、スルホン酸塩基を含有する顔料は、スルホン酸塩基を含有しない従来品に比べ、著しく低粘度である。なお本顔料分散体を3カ月間貯蔵したときの粘度は初期粘度とほとんど変化は認められない。

| 回転数 | 本 顔 料 | | 従 来 品 | |
|----------|----------------|----------------|----------------|----------------|
| | 調製時 | 3 カ月後 | 調製時 | 3 カ月後 |
| 6 r.p.m. | 1 2 2 0 c.p.s. | 1 3 2 0 c.p.s. | 5 5 6 0 c.p.s. | 7 2 0 0 c.p.s. |
| 1 2 | 9 3 0 | 1 0 3 0 | 3 1 2 0 | 4 6 0 0 |
| 3 0 | 4 7 5 | 5 6 0 | 1 3 6 0 | 2 8 5 0 |
| 6 0 | 3 2 5 | 4 0 5 | 8 7 0 | 2 3 6 0 |

実施例 6

例5と同じ要領で4-クロル-2-ニトロアニリン6.9g(0.4モル)をジアゾ化し、ジアゾ化液(I)とする。

一方水2ℓに25℃でカ性ソーダ40gを溶解し、ついでアセトアセト-p-スルホン酸アニライドのカリウム塩11.8g(0.04モル)とアセトアセトアニライド65.5g(0.37モル)を溶解し、90%酢酸72gを加え、液量2.5ℓ、液温15℃に調整し、カップラー液をつくる。このカップラー液に上記ジアゾ化液(I)を加えてカップリング後、濾過、水洗し、沈殿を5ℓの水中に分散し10%塩化カルシウム水溶液40gを加えてレーキ化し、濾過、水洗、乾燥する。収量140g。

本顔料を例5に示したようにニトロセルロース系ビヒクル(固形分17%)にボールミルで分散させたときの分散体(顔料分5.5%)の粘度(BM型回転粘度計、25℃)は、つぎのように、例5の従来品に比べ著しく低い。なお、本顔料分散体を3カ月間貯蔵したときの粘度は、初期粘度とはほとんど変化は認められない。

| 回転数 | 調製時 | 3 カ月後 |
|----------|----------------|----------------|
| 6 r.p.m. | 1 0 8 0 c.p.s. | 1 1 8 0 c.p.s. |
| 1 2 | 9 7 0 | 1 0 8 0 |
| 3 0 | 4 9 5 | 5 8 0 |
| 6 0 | 3 0 8 | 4 0 0 |

実施例 7

例5と同じ要領で4-クロル-2-ニトロアニリン6.21g(0.36モル)をジアゾ化し、液量2.5ℓ、液温0～5℃に調整してジアゾ化液(I)とする。

別にスルファニル酸6.9g(0.04モル)を水200ccに加え、炭酸ナトリウム2gを加え50℃でスルファニル酸を溶解する。これに35%塩酸12.5g(0.12モル)および氷水を加え、液

量300cc、液温5℃に調整し、同温度で40%亜硝酸ナトリウム7gを加えてジアゾ化し、過剰の亜硝酸をスルファミン酸で消去する。液量400cc、液温0～10℃に調整し、ジアゾ化液(II)とする。

2ℓの水に20℃でカ性ソーダ40gを溶解し、アセトアセトアニライド76g(0.43モル)を加えて溶解し、90%酢酸72gを加え、アニライドを析出後液量2.5ℓ、液温15℃に調整する。この液に上記ジアゾ化液(II)を加えてカップリングを行い、ついで上記ジアゾ化液(I)を加えてカップリングを行う。濾過、水洗後、5ℓの水中に再分散し、炭酸ナトリウムを加えてpH8.0～8.5に調整したのち、85℃に加熱し、10%塩化バリウム水溶液60gを加えてレーキ化し、濾過、水洗、乾燥する。収量137g。

別に比較のため、常法に従い、4-クロル-2-ニトロアニリンとアセトアセトアニライドのみをカップリングさせて顔料をつくる。

これら両顔料をライムロジントルエン系ビヒクル(固形分17%)にボールミルで分散させたときの分散体(顔料分7%)の粘度(BM型回転粘度計、25℃)は、つぎのように、スルホン酸塩基を含有する顔料は、スルホン酸塩基を含有しない従来品に比べ、著しく低粘度である。なお、本顔料分散体を3カ月間貯蔵したときの粘度は、初期粘度とはほとんど変化は認められない。

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| 回転数 | 本 顔 料 | | 従 来 品 | |
|----------|----------------|----------------|----------------|----------------|
| | 調製時 | 3カ月後 | 調製時 | 3カ月後 |
| 6 r.p.m. | 1 7 0 0 c.p.s. | 1 8 1 0 c.p.s. | 3 7 6 0 c.p.s. | 5 7 7 0 c.p.s. |
| 12 | 1 0 8 0 | 1 1 8 0 | 3 0 1 0 | 5 0 2 0 |
| 30 | 4 7 6 | 5 7 0 | 1 0 3 0 | 3 0 4 0 |
| 60 | 3 2 0 | 4 0 0 | 5 7 6 | 2 1 8 0 |

実施例 8

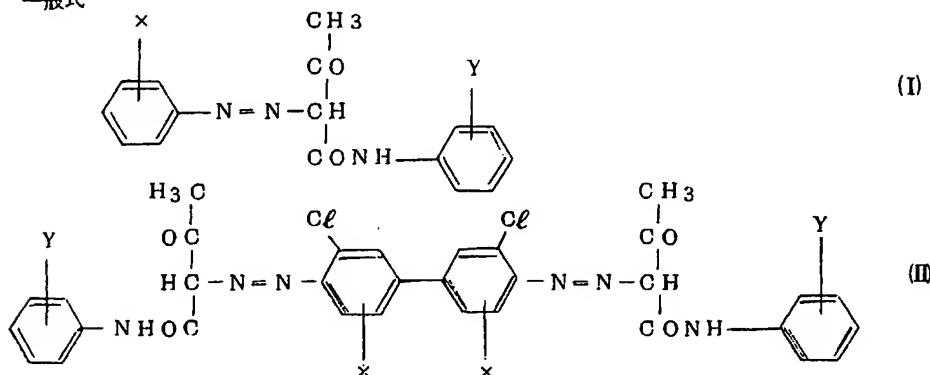
例1と同じ要領で、3,3'-ジクロロベンジン塩酸塩55.5g(0.17モル)のテトラゾ化液(I)をつくる。また例1と同じ要領でアセトアセトアニライド65.5g(0.37モル)の酢酸溶液を液温20℃、液量2ℓに調整しカップラー液とする。これにテトラゾ化液(I)を0~5℃で加えてカップリングを行い、顔料スラリー(II)を得る。別に水300ccに炭酸ナトリウム3gを60℃で溶解し、これに3-アミノ-4-メトキシベンゼンスルホン酸12g(0.06モル)を溶解し、ついで35%塩酸18.8g(0.18モル)を加えて上記スルホン酸を析出させる。氷水を加えて液温5℃とし、同温度に保ちながら40%亜硝酸ナトリウム水溶液10.3g(0.06モル)を加えてジアゾ化し、過剰の亜硝酸をスルファミン酸で除去し、ジアゾ化液(III)とする。また別に水300ccにカ性ソーダ6gを加えて溶解し、これにアセトアセト-0-トリルダイド12.6g(0.066モル)を溶解し、90%酢酸10gを加えてトリルダイドを析出させ液量600cc、特許請求の範囲

液温25℃に調整する。この液に上記ジアゾ化液(III)を加えてカップリング後、濾過し、沈殿を1.5ℓの水に再分散し、炭酸ナトリウムでPH8.0~8.5に調整後50℃に加熱し、アニリン酢酸塩9.2gを水100ccに溶解した液を加えてレーキ化し、顔料レーキ(IV)とする。これを上記顔料スラリー(II)に加え、濾過、乾燥する。収量125g。

本顔料を例2に示したようにニトロセルロース系ビヒクル(固形分17%)にボールミルで分散させたときの分散体(顔料分5.5%)の粘度(BM型回転粘度計、25℃)は、つぎのように例2の従来品に比べ著しく低い。なお、本顔料分散体を3カ月間貯蔵したときの粘度は、初期粘度とはほとんど変化は認められない。

| 回転数 | 調製時 | 3カ月後 |
|----------|----------------|----------------|
| 6 r.p.m. | 1 6 0 0 c.p.s. | 1 9 0 0 c.p.s. |
| 12 | 1 0 1 0 | 1 1 2 0 |
| 30 | 6 0 0 | 7 0 0 |
| 60 | 4 2 0 | 4 6 0 |

1 一般式



(ただし、式中XおよびYはH、CH₃、Cl、NO₂およびOCH₃の群から選ばれた1個以上の置換基を意味する)

で表わされる顔料(I)もしくは(II)またはそれらの混合物または有機アミン塩を混有せしめることを特徴化合物に(I)または(II)のスルホン酸のアルカリ土金属 45 とする黄色アゾ系顔料の製造法。